PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

Ian Anthony JONES, et al.

Appln. No.: 10/666,264

Confirmation No.: 7763

Filed: September 19, 2003

For: WELDING METHOD

Docket No: Q90171

Group Art Unit: 1725

Examiner: Maria Alexandra Elve

DECLARATION UNDER 37 C.F.R. § 1.132

Mail Stop Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, Ian Anthony Jones, hereby declare and state:

THAT I am a citizen of the United Kingdom;

THAT I have received the degree of MA in Natural Sciences from the University of Cambridge;

THAT I have been employed by TWI Ltd since 1989, where I hold a position as a project leader, with responsibility for Polymer Technology;

THAT my financial interest in the present Application has been assigned to The Welding Institute;

THAT I have reviewed U.S. Patent Application No. 10/666,264, filed September 19, 2003, including the Office Action of June 28, 2006 and the disclosures of Corrsin (U.S. Patent No. 3,477,194) and Muellich (U.S. Patent No. 5,893,959), which are relied upon by the

Examiner in the Office Action. As a result of my detailed review of the above items, I make the following observations.

A. Disclosure of an understanding of the features differentiating an organic radiation absorber from an inorganic absorber related to their use in welding of plastics

U.S. Patent No. 3,477,194 of 11 Nov 1969 to Lester Corrsin describes the use of carbon and gypsum as radiation absorbers between two sheets of plastic film. Both are examples of inorganic pigments that could be applied as an ink. He also mentions the use of a visually transmissive absorber (polybutadiene) but only in relation to use with a CO_2 laser with a long infrared wavelength of 10,600 nm.

U.S. Patent No. 5,893,959 of 24 Sep 1996 to Vitus Meullich describes the use of transmission laser welding to join two visually opaque parts. One part contains a laser absorbing 'black dye pigment' (only carbon is mentioned) and the second part contains 'dye pigment' which is laser transmissive. Both parts are visually opaque so as to offer a visually homogeneous impression. Note that the terminology 'dye pigment' is somewhat misleading as is discussed below. This patent is in contrast to the patent application serial number 10/666,264, where no coloration of the parts to be joined is called for and indeed the method is described to join the parts without altering their appearance.

The transmission laser welding process is described firstly, its benefits and why it cannot be carried out with a CO_2 laser.

Further, the selection of radiation absorbers for transmission laser welding will be described highlighting the difference between use of an organic and inorganic absorber, also highlighting the differences between dyes and pigments. Experimental work using gypsum as a radiation absorber is described.

In particular, Andrus (5,093,147) discloses an organic dye that fluoresces under laser radiation. In contrast to the requirement of the organic dye of the patent application serial number 10/666,264, this dye does not generate heat therefore could not effect a weld. Further, as mentioned above, there is no mention in the specification of the use of this dye for welding.

1. The Transmission Laser Welding Process

To achieve a weld between plastics, the joint may be exposed to a beam of radiation from a source, such as a laser, an infrared lamp, or the like. In transmission laser welding of plastics, for instance, the laser beam is directed through the upper plastic layer to the interface between the two parts. It is arranged for an absorber for the laser beam to be present at the interface. Upon irradiation the absorber generates heat in order to melt and fuse the two parts. This is shown schematically in Figure 1.

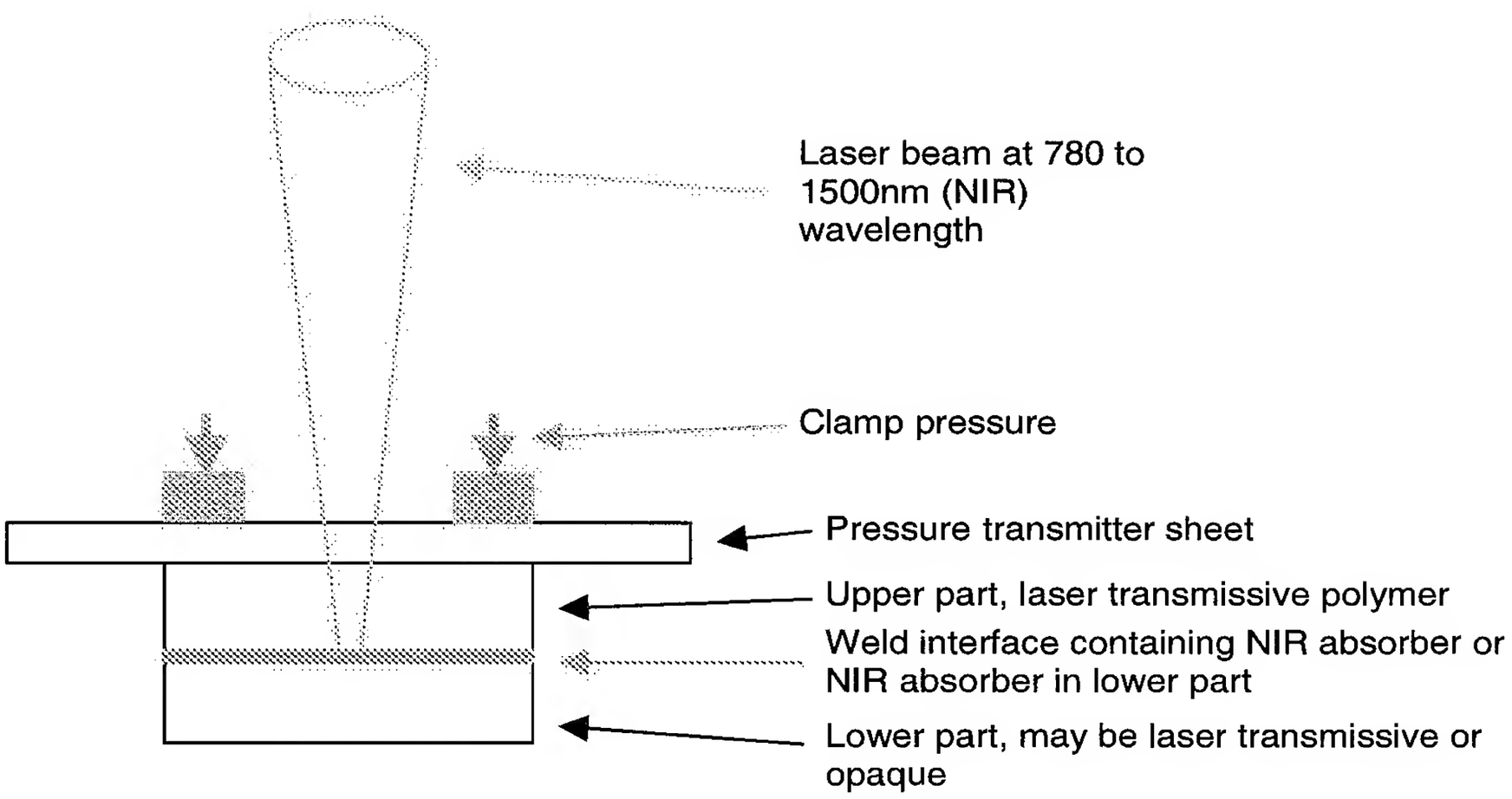

Fig. 1 - Schematic drawing of the transmission laser welding process where the location of the weld interface is shown.

One of the prerequisites of the process is that the upper layer transmits radiation from the laser. The transmission spectrum for polycarbonate, which for these purposes can be considered as a typical polymer, is shown in Figure 2. It may be seen that the transmission in the range 400-1500 nm wavelength is very high, and in other regions including at the 10,600 nm wavelength of the CO_2 laser the transmission is lower, generally much lower. Therefore a CO_2 laser is not

suitable for transmission laser welding and **a laser with a wavelength in the range 780-1500 nm must be selected if the user is to be able to carry out transmission laser welding.**

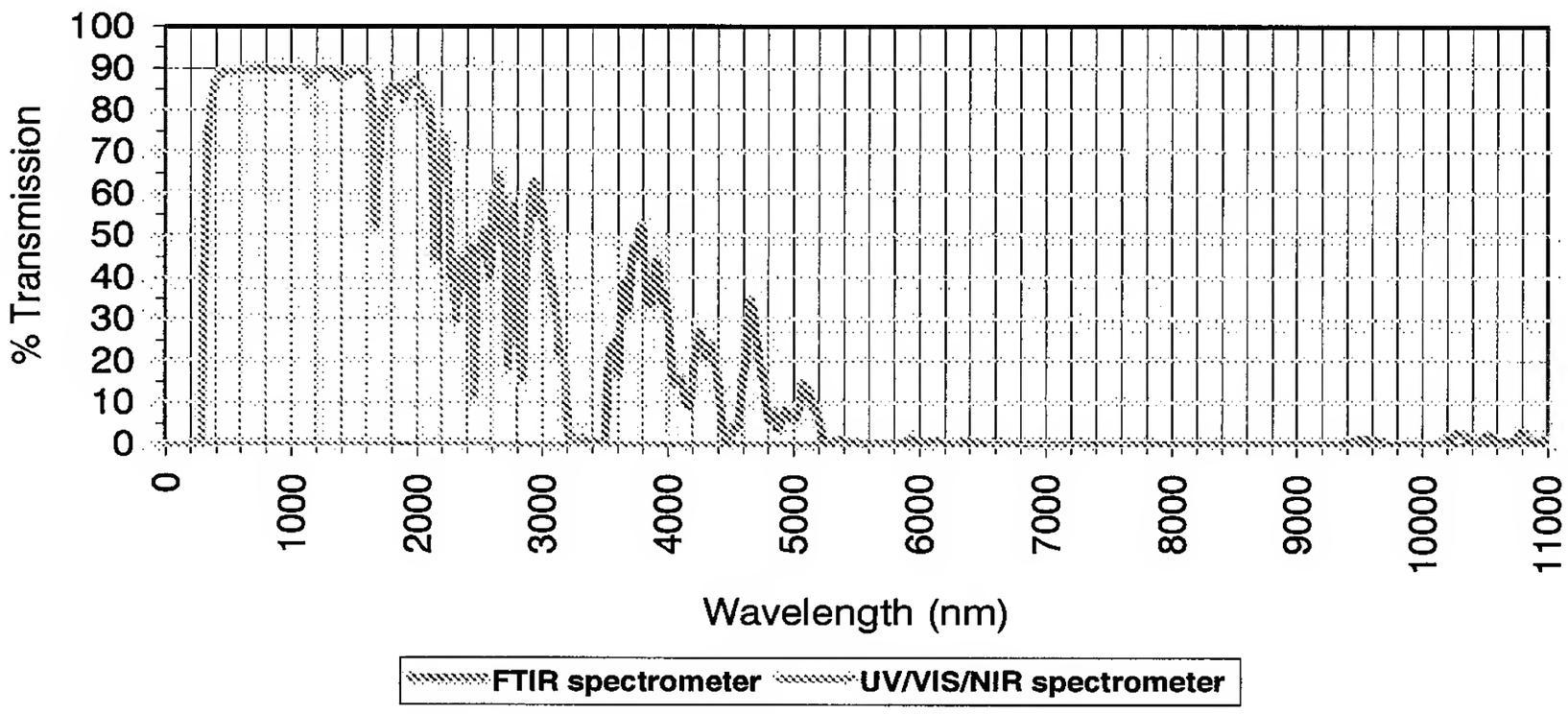

Fig. 2 - Transmission spectrum of polycarbonate.

The use of transmission laser welding enables the user to weld parts at a location a number of millimeters below the upper surface without melting that upper surface. The laser energy is transmitted to the location where it is required. This allows a wide variety of moulded and sheet plastic parts to be welded.

Therefore, the wavelength range (780-1500 nm) selected in the patent application serial number 10/666,264 cannot be described as a specific embodiment of an otherwise wide selection of available wavelengths. This is the only wavelength range that can be used for the transmission laser welding method.

2. Organic and Inorganic Radiation Absorbers

The Corrsin patent refers to the use of carbon and gypsum as radiation absorbers. Both are inorganic materials. The Meullich patent refers to the use of 'black dye pigments' which are either transmissive or absorbing at the NIR radiation wavelength. The only 'dye pigment' absorber mentioned in the Meullich patent is carbon. The patent application serial number 10/666,264 refers to the use of dyes as an absorber which are organic and which contrasts markedly in its appearance and performance in use. The main properties of the materials are given in Table 1.

Table 1 - Summary of properties of organic and inorganic radiation absorbers

	Organic Absorber		**Inorganic Absorber**	
Example	Polybutadiene	Organic dye e.g. squarylium dye; Gentex A195 dye	Carbon	Gypsum
Form	Polymer	Organic molecule usually used in dissolved form. Termed '**dye**'	Black particulate. Termed '**pigment**'.	White particulate. Termed '**pigment**'.
Solubility in polymer host	Poor solubility in most other polymers	Dissolves in most polymers	Insoluble, remains as particle form in polymer	Insoluble, remains as particle form in polymer
Effect of solubility	Does not weld to other polymers, but could act like an adhesive	Molecule does not scatter light; it absorbs light. Transparent polymers remain transparent	Particles absorb light. Polymers become opaque and black.	Particles scatter light. Polymers become translucent or opaque and white.
Absorption spectrum	Minimal absorption in NIR region, high absorption at longer wavelengths	Spectrum has distinct peaks and troughs in NIR region	Spectrum has a monotonic variation	Spectrum has a monotonic variation

Absorption Spectrum response	Cannot be used as an absorption medium for transmission laser welding of polymers because it has similar absorption characteristics to other polymers in not absorbing light in the NIR region of current interest	Absorber properties can be tailored to provide high absorption at the applied radiation wavelength in preference to visual radiation for example	Absorber has some absorption over a wide range of wavelengths. It is not possible to use the material to provide absorption at the laser wavelength in preference to a visible wavelength. So if it is added to promote welding it will also add visible color.	Absorber has some absorption over a wide range of wavelengths. It is not possible to use the material to provide absorption at the laser wavelength in preference to a visible wavelength. So if it is added to promote welding it will also add visible color.
Thermal stability	Melts and then thermally degrades.	Molecules often alter when subjected to welding temperatures.	Unchanged under plastics welding conditions.	Unchanged under plastics welding conditions.

More detail in relation to these properties is given below.

In the patent application serial number 10/666,264, absorber dyes are described as being used to weld the plastic parts together. In the descriptive section of this application, several families of such dyes are listed and all of them are organic dyes. It is thus useful to examine what characteristics pertain to the spectral scans of these dyes used for the purpose of enabling plastics to be welded using near infrared lasers, what makes these characteristics substantially different from analogous characteristics of inorganic pigments or organic dyes lacking or waning in such characteristics, and how the method described in the 264 application called for an aligning or matching of these characteristics to the wavelength reality of the laser beam used.

The following spectrums illustrate Absorption in the NIR (near infrared) with very high transmission in the visible range. This is delivered by a Squarylium Dye (Fig 3a) or A195 (Fig.3b) in Polycarbonate with absorption in the NIR from about 800 through 900 nm or 800 through 1100nm respectively.

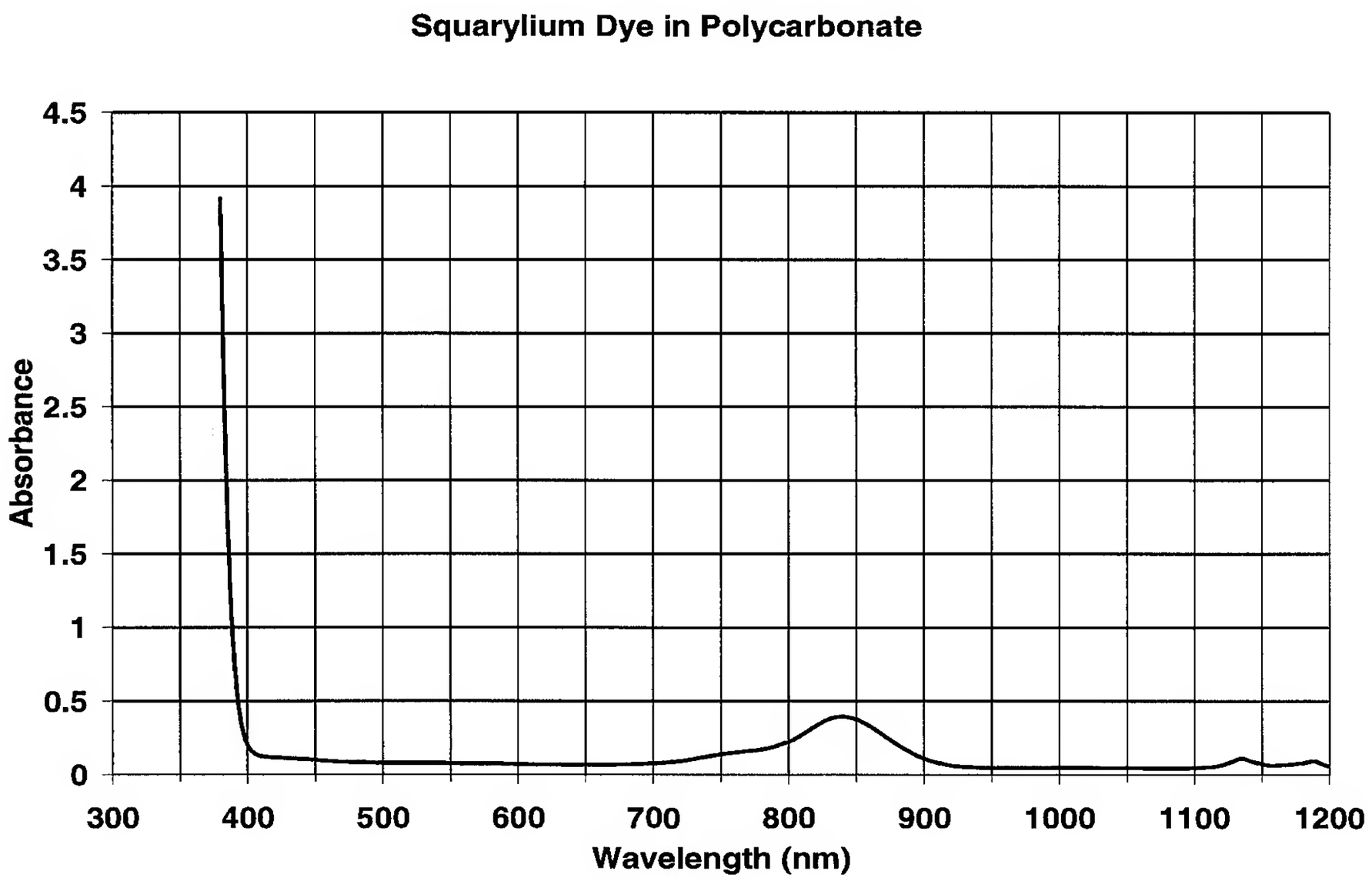

Fig. 3a - Absorbance spectrum for squarylium NIR absorbing dye in polycarbonate.

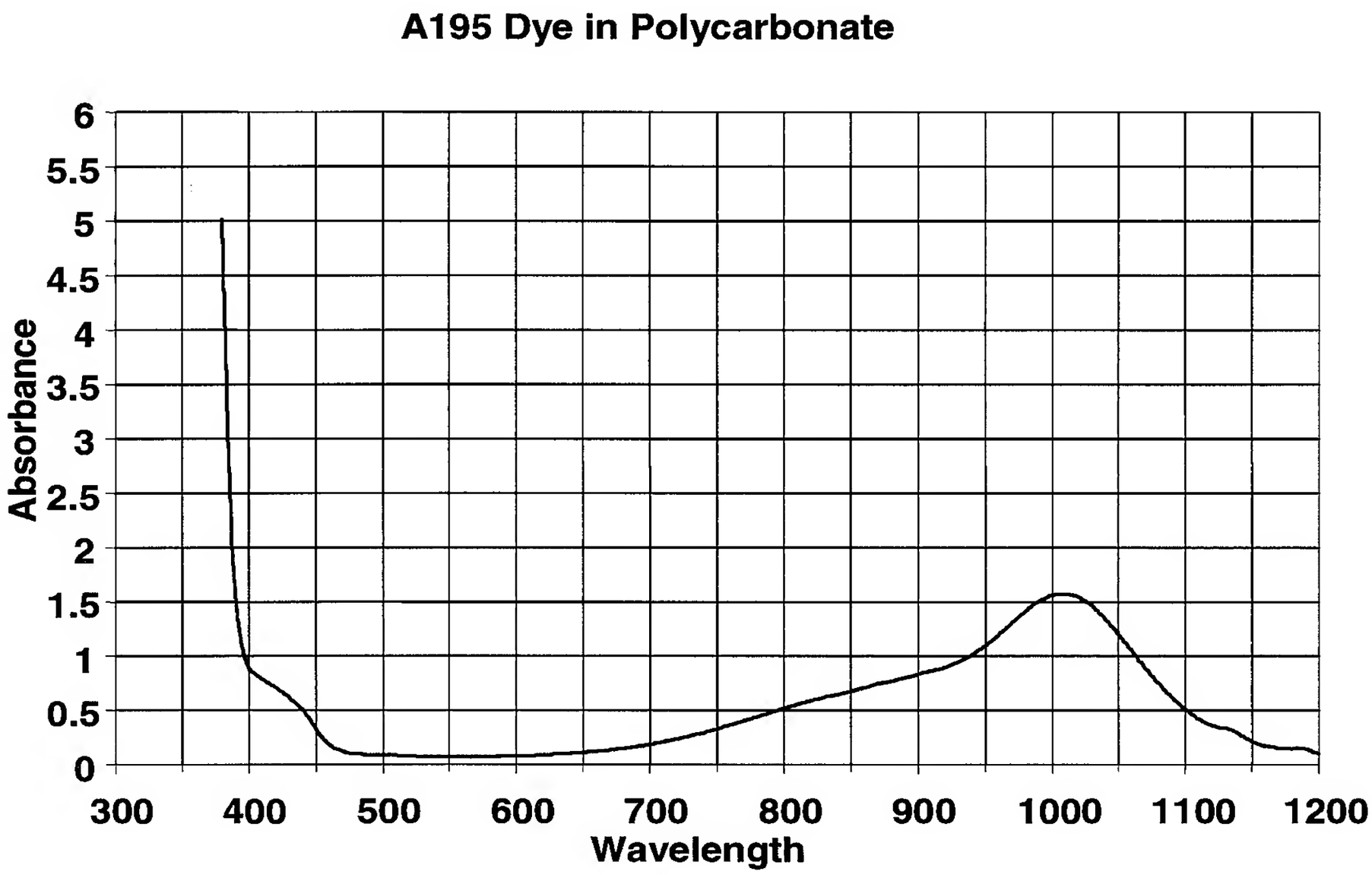

Fig.3b Absorbance spectrum for A195 NIR absorbing dye in polycarbonate.

The following spectrum (Fig. 4) is for a vacuum deposited Carbon (i.e. inorganic) film deposited on a Mylar polyester film. It illustrates the relatively featureless visible and NIR regions as spoken to in this discourse.

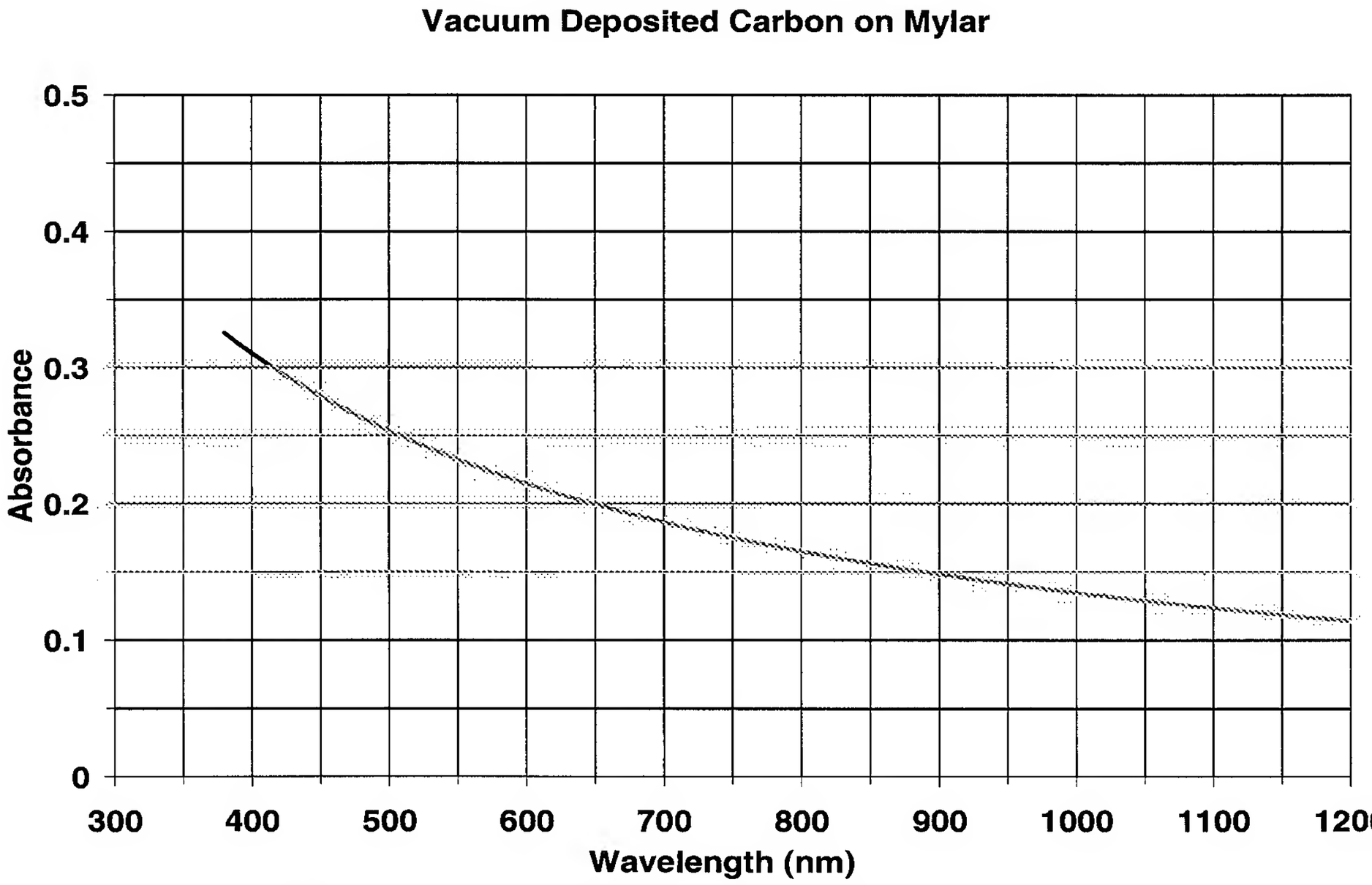

Fig. 4 - Absorbance spectrum for vacuum deposited carbon on mylar (PET polymer film).

The spectrum for gypsum (an inorganic) is shown below (Fig. 5). All were taken between layers of clear acrylic. These again are relatively featureless curves when the overlying effect of the acrylic is ignored.

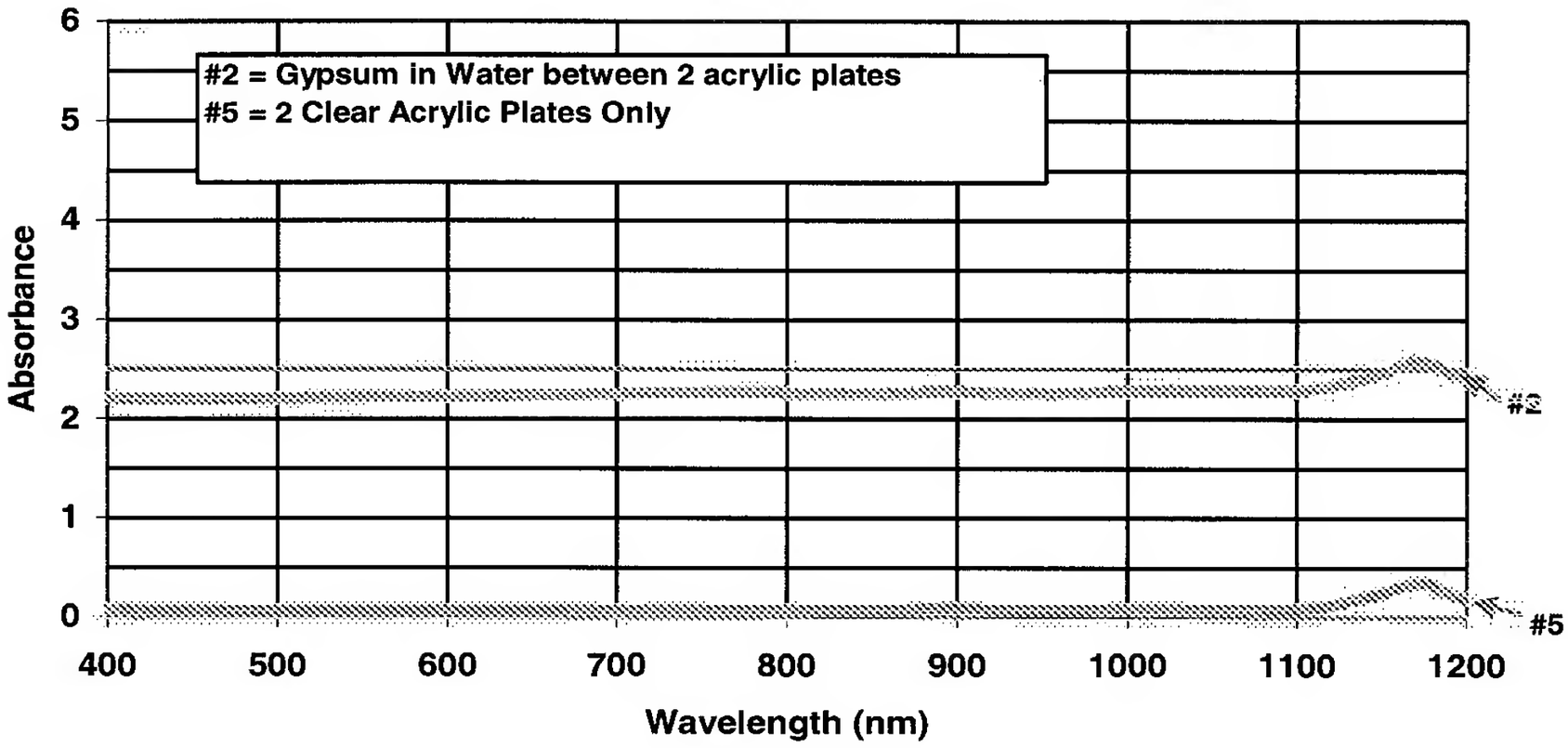

Fig. 5 - Absorbance spectrum for gypsum in water between acrylic plates.

The absorbance spectrum shown in Fig. 6(a) is that of an unpigmented copolymer of styrene and acrylonitrile with polybutadine particles dispersed in it (Usually termed ABS). This is described by Corrsin as a selective absorber at a wavelength of 10.6 microns. This spectrum shows that it is not an absorber in the NIR range 780-1500 nm and is therefore unsuitable as an absorber for transmission laser welding of plastics. It may also be concluded that the polybutadiene constituent is also non-absorbing in the range 780-1500 nm.

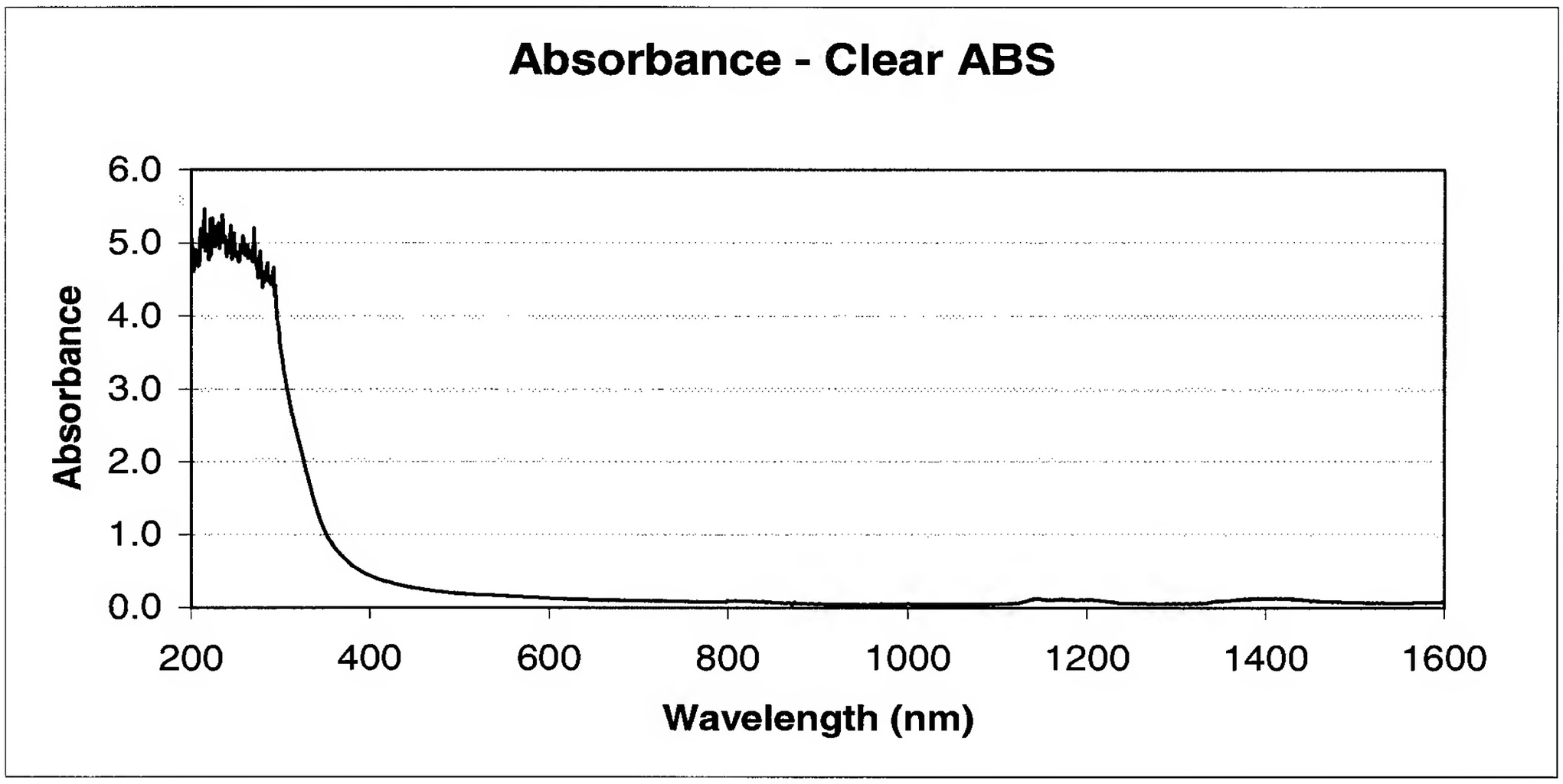

Fig. 6(a) - Absorbance spectrum for acrylonitrile-butadiene-styrene, one of the materials described by Corssin as a selective absorber at 10.6 microns. This material contains polybutadiene and the spectrum shows that it is not an absorber in the NIR range 780-1500nm.

The absorbance spectrum shown in Fig. 6(b) is that of polybutadiene described by Corrsin as a selective absorber at a wavelength of 10.6 microns. This spectrum shows that it is not an absorber in the NIR range 780-1500 nm, but absorbs well at the CO_2 laser wavelength (10,600nm) where transmission laser welding is not effective.

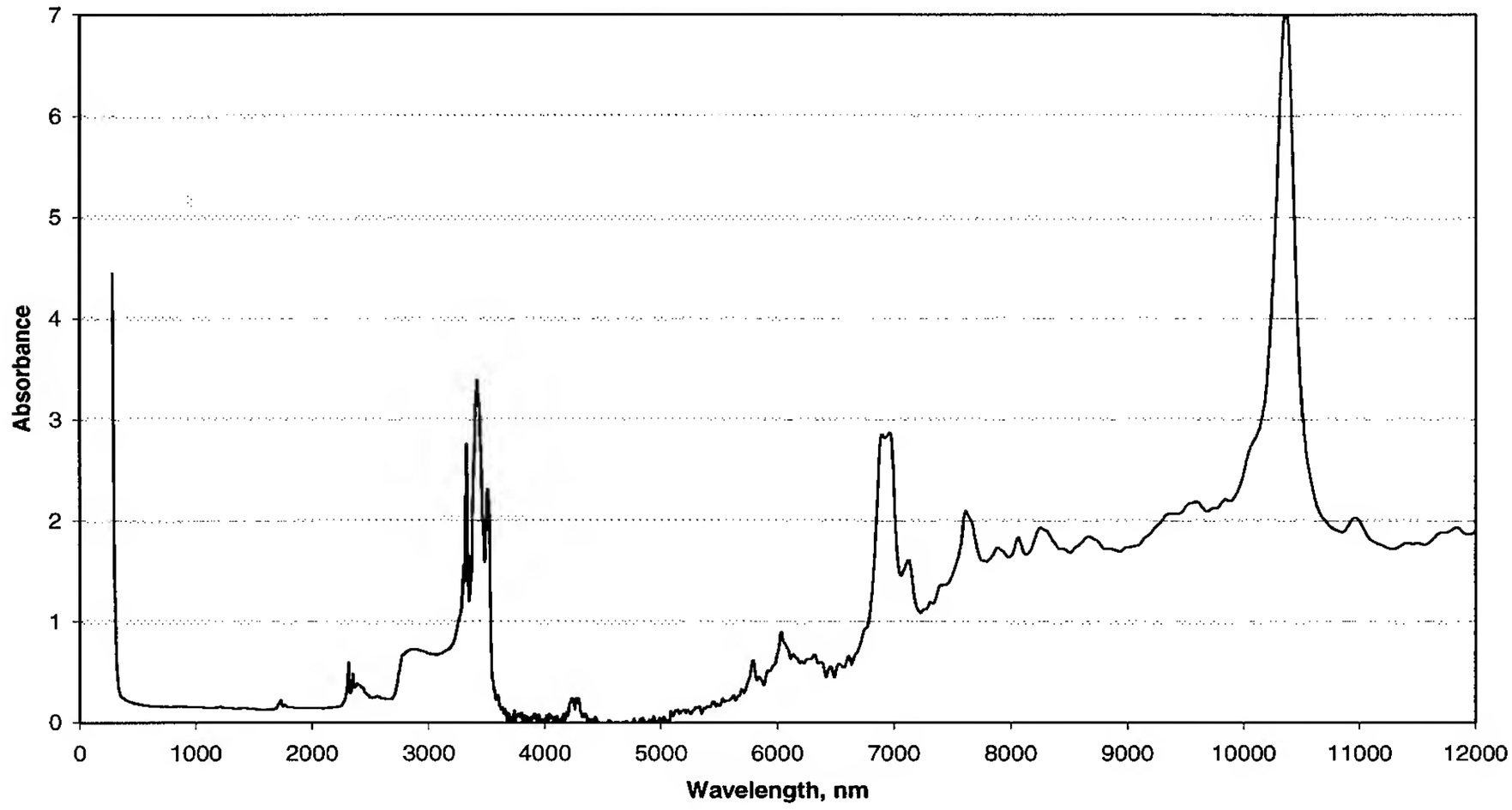

Fig. 6(b) - Absorbance spectrum for polybutadiene.

As one readily notes when looking at these spectral graphs, in the range 400-1500nm (visible through to NIR), the spectra rather naturally divide into two sets –

The First set which has spectra with maxima, minima, saddle points, rapidly varying features, etc. – lots of variation in the spectral curve. It is clear and easy to state that such an absorber is especially suited by virtue of where its maxima, minima, etc. to absorb light in certain specific spectral regions and not very suited to absorb light well in other spectral regions.

A Second set which has spectra with rather gradual monotonically increasing or decreasing characteristics, virtually devoid of the uniqueness factors such as maxima, minima, etc. – not much variation in the spectral features making it difficult or even impossible for one to

say that an absorber in this camp would be substantially better or worse in absorbing light at a target wavelength, for instance say at 980 nm rather than in absorbing at 600 nm.

The First set of absorbers noted above include the types of materials comprised of the organic dyes.

The Second set of absorbers noted above include inorganic species commonly used as pigments in the plastic intended to be welded such as carbon or gypsum. The Second set also includes unpigmented polymers or co-polymers such as polybutadiene.

This introduces the opportunity of exploring the dyes vs. pigments issue rather logically as well. A 'Dye' is a material that dissolves in the substrate – this means that the introduced dye is present as the smallest unit, which characterizes the dye, namely the dye molecule per se. Present as the molecule in the substrate, the dissolved dye is most efficiently capable of absorbing the laser light. By contrast, a 'Pigment' is a material that does not dissolve in the substrate but remains suspended in the substrate as macroscopic agglomerates of composite molecules or ions. As suspended undissolved particles, these suspended pigment particles scatter light very readily and this is evidenced by the fact that such species in polymers are hazy to the eye due to this scattering. Examples of pigments are represented in spectral examples in Figures 4 and 5 above. While scattered light can generate enough heat to effectuate a plastic weld, the efficiency of doing so is much less than via light absorbed by dyes which is very efficiently converted to heat, and the penalty paid in pigment use is that the pigments may introduce haze which affects the visible appearance of the plastic including the welded region. While the

molecules on the surface of a pigment particle can absorb light and convert same to heat, the molecules on the particle's surface are but a tiny fraction of those in the particle's interior where they are inaccessible to incoming light, hence the inefficiency of conversion of absorbed light to heat with the potential penalty of the visual effect of haze caused by the pigment particles' scattering of the light. Scattering may be understood as a process of reflection from particle surfaces. In itself this does not generate heat but will increase the path length that light takes in a material. So if the material absorbs the radiation, slightly enhanced heating results. However, this is an inefficient and imprecise way of generating heat. Organic dyes are very efficient converters of radiation to heat (via absorption).

A pigment like Carbon does not dissolve in any known organic polymer, the carbon molecule being essentially the entire macroscopic carbon pigment particle. A pigment like gypsum ($CaSO_4 \bullet 2H_2O$) is composed of ions, the calcium ion Ca^{+2} and the sulphate ion SO_4^{-2} and H_2O molecules. These ions being ionic are not soluble in the organic polymers of current interest, which are not ionic in nature. This same argument can be extended to other similar inorganic species, which are comprised of inorganic ions and/or inorganic macromolecular ensembles (like Carbon), neither type of which will dissolve in organic polymers

One can readily see that, in order to implement the transmission laser welding process in such a way as to avoid substantially altering the appearance of the parts being welded, the material exhibiting matched properties must provide characteristics such those described in

application serial number 10/666,264, which would not be disclosed by Corrsin or Muellich at least for the reasons discussed above.

B. Disclosure of details of experimental practice related to the use of Gypsum as a an absorptive consumable for laser welding plastics

The aim of this work was to reproduce the results described by Corrsin. The relevant section from the Corrsin patent is reproduced here (US '194 Col 4, lines 16-46):

"By way of example, pigmented polyethylene 3 mils thick is heat-sealed to transparent polypropylene according to the present invention. The polyethylene is coated in the areas to be sealed with a radiation absorber which will selective absorb radiation in the near infrared from 1 to 3 microns. An incandescent source such as a tungsten filament provides such radiation. The selective absorber is made by preparing an aqueous suspension having in the range from 10% to 15% total solids by mixing a suitable amount of gypsum ($CaSO_4.2H_2O$) with a suitable amount of water using calcium oleate as a dispersant. From 0.1 to 0.3% by weight of the oleate is used, based on the weight of the gypsum.

The coating is placed on the areas to be sealed and dried. The article to be packaged is placed at the appropriate point on the polyethylene film. The polypropylene film is laid thereover, preferably in such a manner as to bring the polypropylene in direct contact with the dried residue of the coating previously prepared, applied and dried. The polypropylene film is disposed between the pigmented polyethylene and the infrared source.

The above structure is exposed to infrared radiation for a time sufficient for the calcium sulphate, which effectively absorbs radiation in the near infrared from 1 to 3 microns, to absorb sufficient heat energy from the incandescent source to bring the sealing of the polypropylene to the polyethylene."

1. Experimental Practice

This procedure was carried out by Marcus Gordon, an employee of The Welding Institute, under my supervision.

Gypsum powder ($CaSO_4.2H_2O$) was sourced from Sigma Aldrich. The material was a white powder.

Calcium oleate was sourced from Sigma Aldrich. The material was a thick clear yellow paste. 15 g of the gypsum powder was added to 85 ml of water. 0.03g of calcium oleate was added to the gypsum and water and thoroughly mixed.

The resulting mixture was a thin white suspension from which the gypsum settled in a minute or so.

Low density polyethylene film was used to prepare five sample types for welding trials using an infrared tungsten filament lamp (Research Inc., Hotspot model 4085). Both clear polyethylene film (100 μm thick) and black polyethylene film (carbon pigmented, 70 μm thick) were used in the samples. Polyethylene is expected to give more effective results when welded to itself rather than to polypropylene. In some samples the surfaces to be joined were scuffed with

fine sandpaper to improve the wetting of the gypsum suspension although this is not suggested in Corrsin.

A small quantity of the gypsum suspension (which was first shaken to disperse the gypsum pigment) was applied to the surface of clear polyethylene. The coating was spread to a thin layer using an overlaid film of polyethylene, which was pressed and removed. On polyethylene that was not scuffed, the coating quickly formed into islands up to 20 mm across indicating poor wetting of the film (see Fig 7). Scuffing the polyethylene before coating in the same manner led to improved wetting though still not to an evenly deposited coating.

The coatings were dried in ambient laboratory conditions.

After coating with the gypsum suspension, the coated regions of the clear polyethylene had an obvious white coloration. This was also very obviously visible when the coated film was placed over a black-pigmented film.

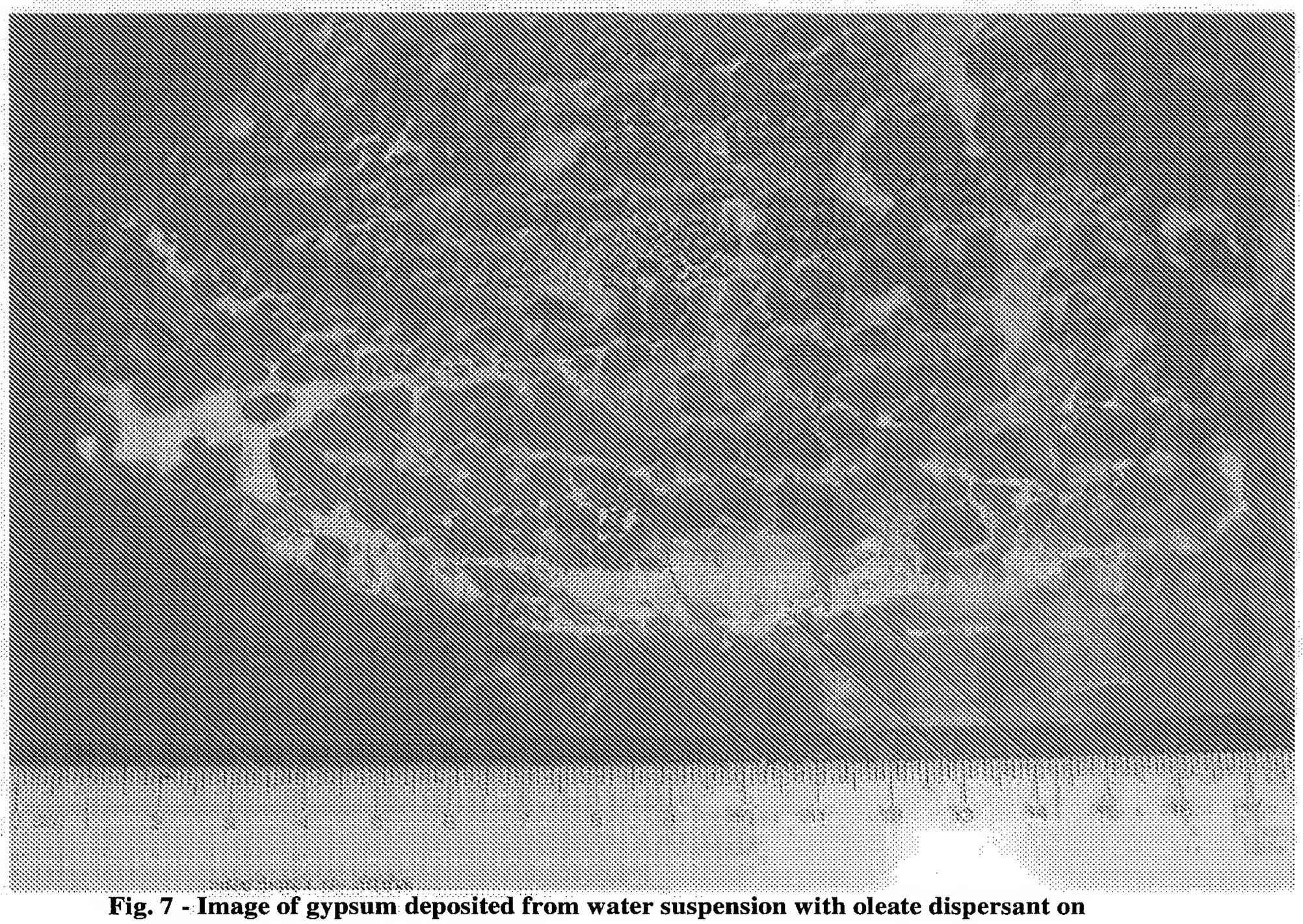

Fig. 7 - Image of gypsum deposited from water suspension with oleate dispersant on polyethylene film. Black background.

The samples were placed on a flat aluminum table, mounted below the infrared lamp. The lamp was used at its focus position with a spot size of approximately 5 mm. To improve the interface contact, the films were pulled tight over copper tubing. For each sample type the samples irradiated in a fixed position beneath the lamp for times from 1-5 secs with the aim of finding a suitable condition to make a spot weld. The lamp power was 750W.

The following samples were prepared. An indication of the result achieved is given in each case:

1. Clear to black carbon pigmented polyethylene film (not scuffed) with no gypsum coating. Successful weld achieved.
2. Clear to black carbon pigmented polyethylene film (scuffed) with gypsum coating applied as described above. No weld achieved.
3. Clear to clear polyethylene film (not scuffed) with no gypsum coating. No weld achieved.
4. Clear to clear polyethylene film (not scuffed) with gypsum coating applied as discussed above. No weld achieved.

5.Clear to clear polyethylene film (scuffed) with gypsum coating applied as described above. No weld achieved.

6 Clear to clear polyethylene film (scuffed) with no gypsum coating. No weld achieved.

The gypsum coating gave a visible white appearance to the polyethylene film present before and after irradiation by the lamp.

Clear to clear samples with a gypsum coating were also irradiated with a laser heat source. A 940 nm wavelength diode laser source was used at a power of 100W and a spot size set to 5 mm wide. The films were clamped beneath an acrylic cover sheet using a sliding ring clamp, through which the laser beam was passed. Speeds between 0.3m/min and 5m/min were tested with the aim of finding a suitable linear welding condition. There were no welds achieved with this range of conditions on the clear-to-clear film samples. Conversely, it is known that similar process parameters used with radiation absorbing materials as described by the patent application 10/666,264, would result in a weld of the two work pieces.

2. Conclusions from Experimental Practice

The gypsum does not assist welding of a visually transmissive thermoplastic film to either a pigmented or visually transmissive film. It acted as a barrier to welding considering that the transmissive and pigmented films can be welded successfully without the gypsum coating and cannot be welded when the coating is applied.

The gypsum coating is clearly visible on either a clear uncolored film or on a black pigmented film both before and after irradiation by an infrared heat source.

C. Demonstration of welding with 'black dye pigment' as per Meullich

It is reasonably understood that the absorbing black dye pigment mentioned in the Meullich patent is carbon particulate as this is the only one mentioned in the patent. The

properties of this are described above. The NIR transmissive black dye pigment is a black colorant that does not contain carbon particles. The image below (Fig. 8) shows the appearance of a component laser welded from two parts with the two different black dye pigments as taught by the Meullich patent. Both parts, the case and the set of buttons on the front, appear black to the eye but contain two different colorants, one transmissive and the other absorbing to the laser.

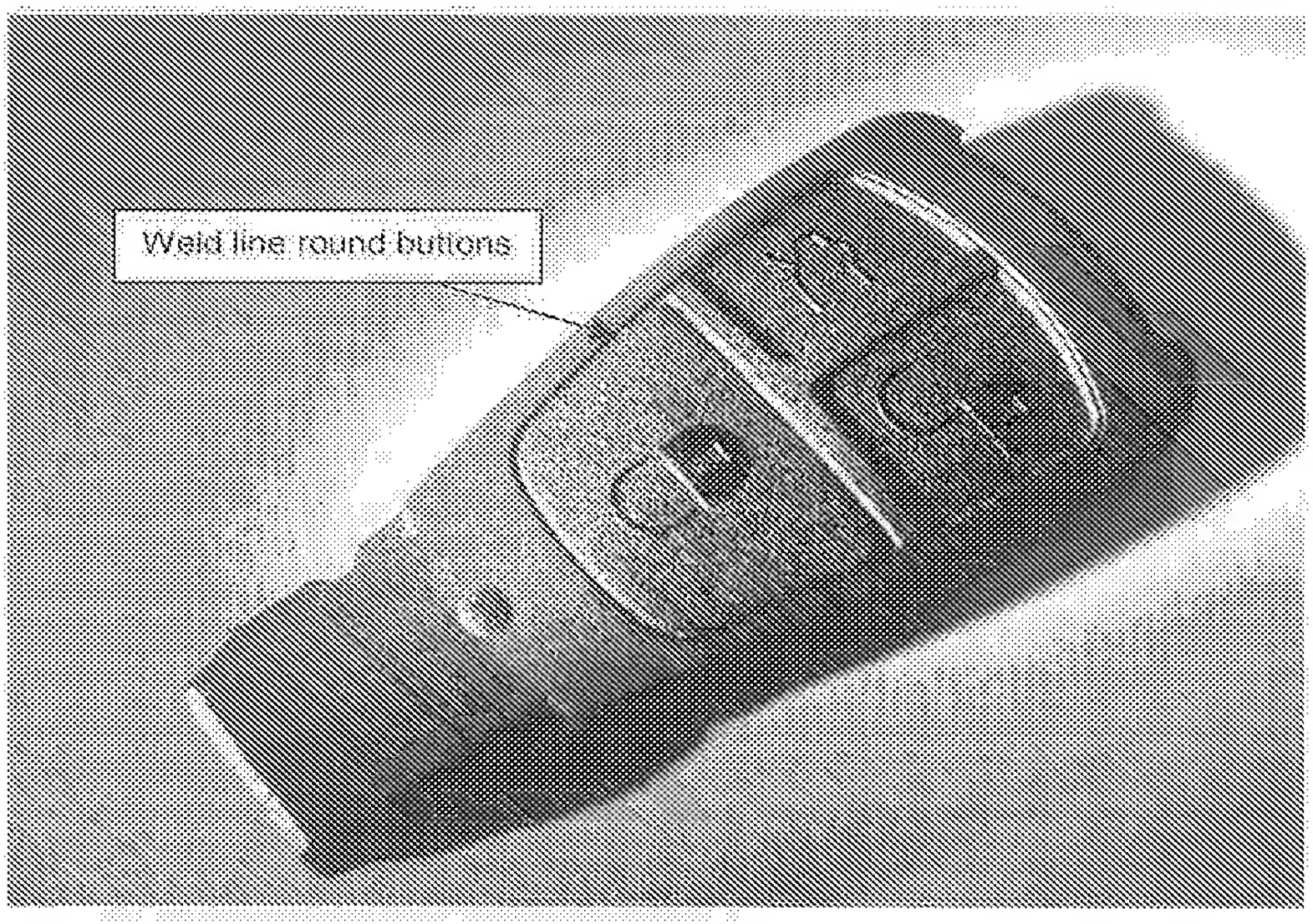

Fig 8 - Parts welded with near-infrared absorbing colorant in one and transmissive black colorant in the other. The weld is round the buttons, both parts appear black to the eye, but one is transmissive to the near-infrared laser to allow welding through it.

This makes transmission laser welding possible for this pair of parts. Carbon is used in the laser absorbing part. Colorants are added to the other parts to provide the same visual appearance as the first part.

This is in contrast to the '264 application in question where a dye is used with very little visible color and it is being used in such a way that the weld can be made without any need to alter the color of the parts, whatever they may be. Figure 9 shows an example of a weld made

between two clear plastic pieces using the innovation described in the '264 application. For contrast again this sample is shown with one using carbon black as an absorber to facilitate the welding process. The black colour is clearly visible in the upper sample in Figure 9.

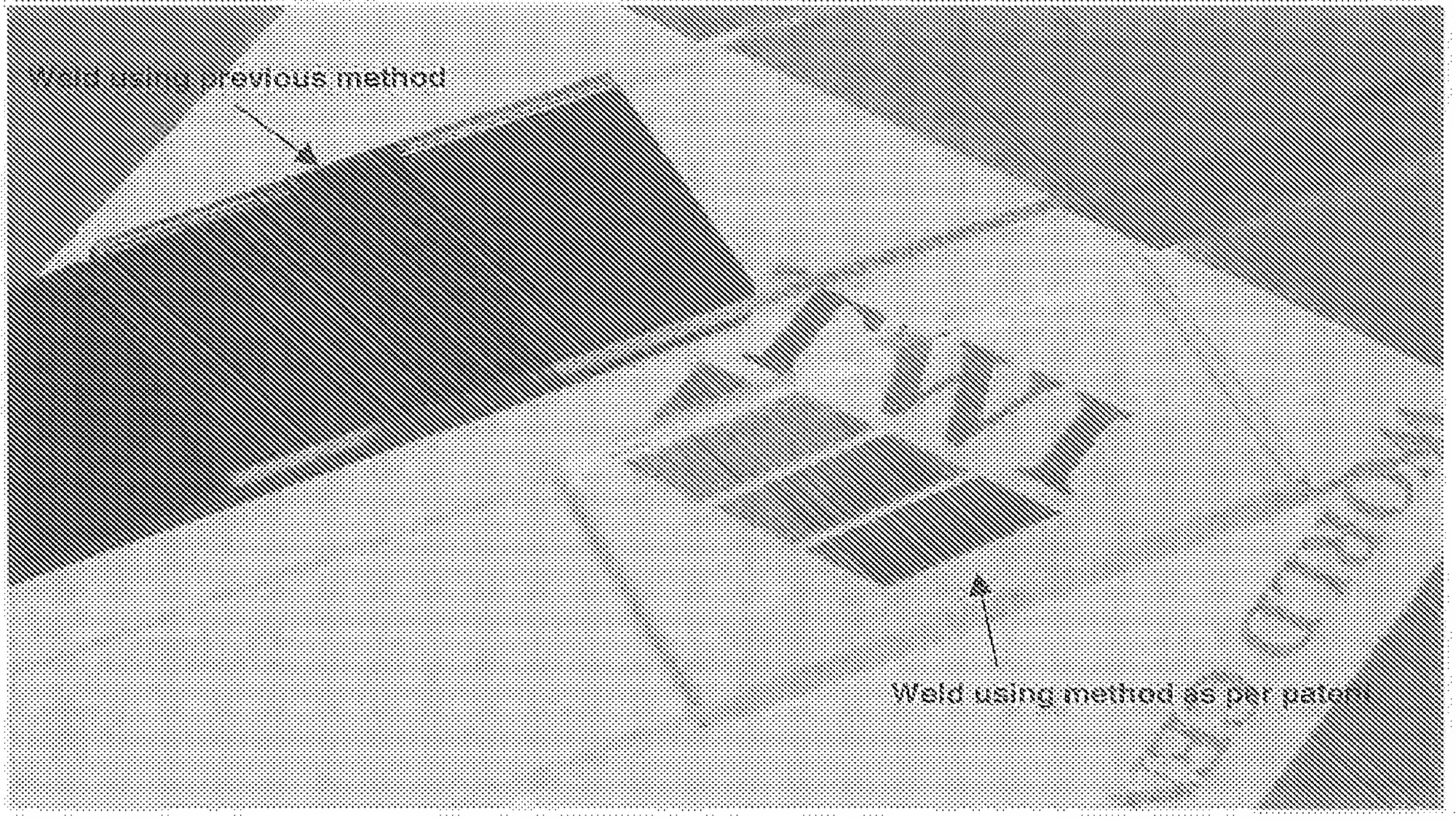

Fig.9 Welds between plastic parts using a carbon black absorber (upper), the state of the art before the patent application 10/666,264, and using the absorber described by the said patent application to make a joint without significantly affecting the visible appearance (lower).

D. The Lack of Potential for Fluorescing Dyes to Generate Heat Sufficient for Welding

Andrus (5,093,147) discloses an organic dye that fluoresces under laser radiation. In contrast to the requirement of the organic dye of the patent application serial number 10/666,264, this dye does not generate heat therefore could not effect a weld. The reasoning behind this statement is discussed below.

When a dye absorbs light at any wavelength, it escalates/excites from its initial ground state to an excited electronic energy state. From there (1) it can re-emit that absorbed light at that very same wavelength, or (2) it can convert that absorbed energy to heat by vibrationally dissipating it (called a vibrational cascade), or (3) it can transition from its excited electronic state called a singlet state to a slightly lower energy excited triplet state and from there re-emit light of a slightly lesser energy than is absorbed (i.e., re-emit light of a longer wavelength) in going from that triplet state back to the ground state in a process called fluorescence.

Note that in (1) no absorbed energy is converted to heat. In (3) nearly no absorbed light is converted to heat as most of it is re-emitted as fluoresced light (light emitted at a higher wavelength than at which it was absorbed). In (2) one gets the maximum amount of absorbed laser light converted to heat via the noted vibrational cascade. If one were to choose a dye which absorbed laser light at say a near infrared laser wavelength to generate heat for say a polymer welding procedure, then a dye which behaved as (1) would be the worst choice as no heat is generated by which to weld, (3) is a poor choice because most of the absorbed laser light is

fluoresced back to the surroundings with very little heat generated, while (2) optimally would convert the absorbed light to heat to effectuate say a weld. Clearly in choosing a dye to do laser welding of polymers, we would not want one which fluoresced as that represents loss of absorbed energy as re-emitted light which we'd rather have as emanated heat to do the intended welding task. Our choice would be a dye which behaved via mode (2).

In these respects, Examiner Elve's citation is confusing to a skilled man in near infrared absorbers which fluoresce when irradiated with NIR light. It is for this reason that the choice of a fluorescent dye to effect a weld in plastic is confusing and does not make sense.

E. Conclusion

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: 12 Dec 06

Ian Anthony JONES